

Classical mechanics technique for quantum linear response

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It is shown that the lowest excitation energies of a quantum many-fermion system in the random phase approximation (RPA) can be obtained by minimizing an effective classical energy functional. The minimum can be found very efficiently using generalized Lanczos technique. Application of the new technique to molecular spectra allows to compute excited states at the expense comparable to the ground-state calculations. As an example, the first-principle RPA excitation spectrum of C60 molecule is computed taking into account all 240 valence electrons in the full valence space of the molecule. The results match linear absorption experiment within percents.

Random phase approximation is central to the theory of electronic excitations in molecules and in extended systems [1]. More generally, it resides in the core of the theory of linear response of correlated many-particle systems, and is widely used to describe correlation effects in the excitations of nuclei [2,3], molecules [4,5], semiconductor quantum wells [6], quantum dots [7], and bulk materials [8]. Large systems of RPA-type equations are of particular significance in photochemistry of large molecules. Understanding such processes as photosynthesis and light reception in vision requires detailed description of the evolution of large biological molecular complexes upon optical excitation [9], which is governed by the configuration of excited-state adiabatic surfaces [10]. Yet, unlike ground-state molecular calculations, which are now considered a routine job with the powerful program packages at hand [11], the modeling of the excited states is a much more difficult task [12].

The reason behind this difficulty is that *electronic correlations* are usually much more pronounced in the excited states. In other words, when the ground state electronic wavefunction can be reliably approximated using Hartree-Fock (HF) or density functional theory (DFT), the electronic wavefunction in the excited state cannot be described as a single Slater determinant.

RPA is one of the standard tools to treat electronic correlations in the excited states of quantum many-particle systems. It belongs to a broader family of so-called *time-dependent* techniques, such as time-dependent HF (TDHF) and time-dependent DFT (TDDFT). These methods target directly the excitation energies of the system, by associating these energies with the frequencies of oscillations of the ansatz parameters when the system is driven out of equilibrium. The static HF or DFT ground state is the best Slater determinant that gives minimum to a certain energy functional. The TDHF and TDDFT describe the time evolution of the respective Slater determinant near the equilibrium.

An assumption is made that the time-dependent wavefunction remains a single Slater determinant at each moment in time. Projection of the time-dependent Schrodinger equation onto the set of all Slater determinants yields a set of essentially classical Hamiltonian

equations of motion [1]. In linear response, when the deviation from equilibrium is small, the motion represents small oscillations, whose frequencies are associated naturally with the excitation energies of the system. In the small-oscillation limit TDHF is equivalent to RPA.

RPA excitation energies are obtained as the eigenvalues of a non-Hermitian matrix [2]

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \quad (1)$$

The $N \times N$ symmetric matrices A and B describe particle-particle interaction. Their matrix elements are simple combinations of the two-particle interaction matrix elements of the Hamiltonian in the basis of HF orbitals.

Configuration interaction singles (CIS), which is another commonly used technique to describe correlation effects, is in fact an approximation to RPA, and can be recovered by setting $B = 0$ [4].

In contrast to the static HF, where the number of equations scales linearly with the number of particles, the size $2N$ of the matrix (1) grows quadratically with the size of the single-particle Hilbert space. This impedes diagonalization of the matrix (1) for relatively large systems. For example, RPA equations for the singlet excited states of C60 molecule in the full valence space basis lead to the matrix of the size $2N = 28,800$. On the other hand, complete solution of the TDHF equations is not always necessary. In many cases, only a few low-energy excitonic states are of interest.

This amounts to computing only a few extremal eigenvectors of the matrix (1) — a task similar to a standard problem in quantum mechanics of computing a few low-energy eigenstates ψ of a Hermitian matrix H . The latter problem can be solved very efficiently using Hermitian Lanczos algorithm [13], or any of its various modifications. In essence, the algorithm builds a Krylov subspace \mathcal{K}_n of the matrix H , and then finds the best approximation to ψ in \mathcal{K}_n by minimizing the expectation value of the energy $(\psi H \psi)$ [14].

There exist many variations of the Lanczos algorithm that allow to find eigenpairs of non-Hermitian matrices [14]. These methods, however, lose very much of the

performance of the Hermitian Lanczos algorithm, because of the lack of a *minimum principle*. Indeed, no general minimum principle exists that yields eigenvalues of non-Hermitian matrices [15].

A lot of effort has been put into developing reliable methods for computing selected eigenvalues of RPA-type matrices (1) [16–22]. In [16] the Davidson algorithm has been extended to solve RPA equations as a general non-Hermitian eigenvalue problem. In [17,18] it was modified to preserve the special paired structure of the matrix (1). Tretiak et al. [19] have developed a density-matrix-spectral-moments (DSMA) algorithm based on generalized sum rules for the response theory. The symplectic Lanczos algorithm suggested by Mei [20] and improved by Benner [21] exploits the analogy between the unitary transformations that preserve Hermiticity and the symplectic transformations that preserve the paired structure of (1). A Newton-Raphson-type iterative procedure has been developed in [22]. Finally, the oblique Lanczos algorithm for general non-Hermitian matrices [15] was applied to the TDHF problem in [23].

It has been majorly overlooked that, although the RPA-type matrix is non-Hermitian, its block paired structure gives it some properties similar to the Hermitian matrices. In particular, there does exist a minimum principle that yields the lowest *positive* eigenvalue of (1). It was suggested by Thouless back in 1961 and reads [2]

$$\omega_{\min} = \min_{\{x,y\}} \frac{(x,y) \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}}{|(xx) - (yy)|} \quad (2)$$

The minimum is to be taken over all N -vectors x and y . The minimum always exists, since the HF stability condition keeps the numerator positive [2]. Note, that the denominator can be arbitrarily small, and therefore the expression has no maximum.

The eigenvalue equation for the matrix (1) can be transformed into the form of Hamiltonian equations of motion for classical oscillations by substitution $T = A+B$ and $K = A - B$:

$$Tp = \omega q, \quad Kq = \omega p, \quad (3)$$

Here vectors q and p play the role of the conjugate canonical coordinates and momenta, while K and T are the matrices of stiffness and kinetic coefficients respectively.

The lowest frequency of a harmonic Hamiltonian system can be obtained as a minimum of its total energy over all phase-space configurations $\{p, q\}$ normalized by $(pq) = 1$:

$$\omega_{\min} = \min_{(pq)=1} \frac{(pTp)}{2} + \frac{(qKq)}{2}. \quad (4)$$

Indeed, variation of (4) with respect to p and q yields Hamiltonian equations of motion (3). The minimum

principle (4) is equivalent to the Thouless minimum principle (2), where $x = p + q$ and $y = p - q$.

Two terms in the right-hand side of (4) are the kinetic and the potential energies at the configuration $\{p, q\}$. Both are positive for any p and q when the equilibrium is stable. The positive definiteness of K and T leads to the positive definiteness of the matrix in (2), and thus, to the HF stability condition, making all eigenfrequencies real [24].

Minimum (4) can be easily found using the generalized Lanczos recursion [25]

$$q_{i+1} = \beta_{i+1}^{-1}(Tp_i - \alpha_i q_i - \beta_i q_{i-1}) \quad (5a)$$

$$p_{i+1} = \delta_{i+1}^{-1}(Kq_i - \gamma_i p_i - \delta_i p_{i-1}), \quad (5b)$$

which generates configuration space vectors (q_i, p_i) that span the Krylov subspace of the eigenvalue problem (3). When four coefficients α_i , β_i , γ_i , and δ_i are chosen at each step i to ensure $(q_{i+1}p_i) = (q_{i+1}p_{i-1}) = (p_{i+1}q_i) = (p_{i+1}q_{i-1}) = 0$, the vectors p_i , q_i form a biorthogonal basis, $(p_i q_j) = \delta_{ij}$ and the matrices $\tilde{K}_{ij} = (q_i K q_j)$ and $\tilde{T}_{ij} = (p_i T p_j)$ are symmetric tridiagonal, with the only nonzero matrix elements $\tilde{K}_{ii} = \alpha_i$, $\tilde{K}_{i,i-1} = \tilde{K}_{i-1,i} = \beta_i$, $\tilde{T}_{ii} = \gamma_i$, and $\tilde{T}_{i,i-1} = \tilde{T}_{i-1,i} = \delta_i$. Expanding $q = \sum c_i q_i$ and $p = \sum d_i p_i$, we arrive at the $2n \times 2n$ eigenvalue problem

$$\tilde{T}d = \tilde{\omega}c, \quad \tilde{K}c = \tilde{\omega}d, \quad (6)$$

which has the same structure as (3). The lowest positive eigenvalue $\tilde{\omega}_{\min}$ of (6) give the approximation to the true lowest frequency ω_{\min} . The accuracy is found to improve exponentially with increasing n .

When the lowest-frequency normal mode $q^{(1)}, p^{(1)}$ is found, the second-lowest normal mode $q^{(2)}, p^{(2)}$ can be obtained by choosing initial vectors q_1 and p_1 orthogonal to $p^{(1)}$ and $q^{(1)}$ respectively. As follows from Eq. (4) such a choice causes all vectors q_i and p_i to remain orthogonal to $p^{(1)}$ and $q^{(1)}$. An *oblique projection* can be used to correct for the loss of orthogonality with respect to $p^{(1)}$ and $q^{(1)}$ that may occur at large n . Namely, the necessary amounts of $q^{(1)}$ and $p^{(1)}$ should be subtracted from q_i and p_i respectively to ensure $(q_i p^{(1)}) = (p_i q^{(1)}) = 0$. Higher-frequency TDHF solutions can be found one by one in this way.

In order to demonstrate the power of the new technique, it has been applied to compute the excitation spectrum of the fullerene C60 molecule. Albeit the great attention this molecule has received in the past several years [26], no adequate correlated calculation of the excited-states of C60 has been reported so far.

As noted above, CIS in the entire particle-hole configuration space can be seen as an approximation to RPA, where the matrix B in (1) is neglected. Yet, large size of the molecule has prevented full diagonalization of CIS matrix in the entire space. Calculations for C60 have

been reported using CIS with the CNDO/S Hamiltonian in the truncated space of up to 1295 out of 14400 particle-hole configurations [27], and using TDDFT with B-P86 functional [28]. Also a surprisingly high lowest optically-allowed transition energy of 5.13 eV has been reported using *ab-initio* Rettrup-type RPA calculation [29].

The technique outlined above has allowed to solve RPA equations in the entire valence particle-hole configuration space of the molecule (matrix size $N = 2 \times 14400$). INDO/S semiempirical parameterization of the Hamiltonian [30] was used, which is essentially better than CNDO/S, and was shown to give especially good description of the excitation spectra of π -conjugated molecules at the CIS/RPA level of theory [4,5].

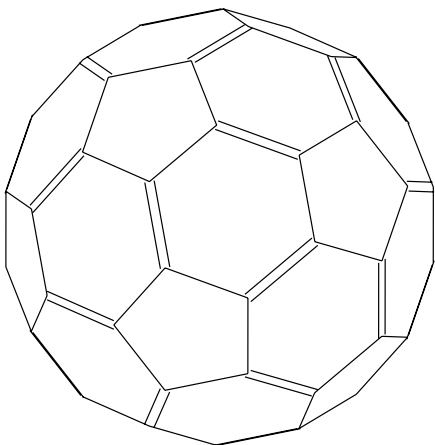


Fig. 1. C60 geometry is completely determined by the single and double bond lengths.

Experimental values of 1.46 and 1.455 Å [26] were chosen for single and double bond lengths respectively, which completely determines the geometry of the molecule (see Fig. 1). INDO/S Hamiltonian matrix elements were generated using ZINDO program [31]. Only the singlet states of C60 were studied. The calculation was performed on DEC Alpha 500au workstation. Solution of static HF equations took about 2 min. CPU time compared to about 6 min. per each excited state.

The present results allow for the first time for the direct comparison to the experiment. As shown in Table I, the energies of optically-allowed transitions obtained are within percents from the features observed in the linear absorption of C60 in solution [32]. In Ref. [28] the modes were found to have a systematic red shift by 0.35 eV. No systematic shift was observed in the present study. Almost perfect match of all transition energies to the features seen in linear absorption allows to resolve the controversy of the assignment of the lowest optically allowed transition towards the value of 2.87 eV, which is opposite to the conclusion of [29].

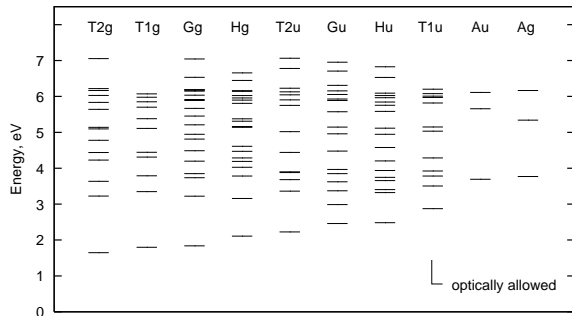


Fig. 2. Excitation spectrum of C60 obtained using TDHF with INDO/S semiempirical Hamiltonian parameterization. Only T_{1u} states have nonzero oscillator strengths.

Fig. 2 shows the complete excitation spectrum obtained. A total of 500 singlet excited states have been computed. The excitation energies were found to be degenerate 1, 3, 4, or 5 times in accordance with multiplicities of irreducible representations of the I_h symmetry group. No symmetry-induced simplification of the problem has been used. A symmetry analysis was performed for each mode after it was computed and the irreducible representation of the symmetry group was assigned.

Table I. C60 Experimental and theoretical electronic excitation energies and experimental oscillator strengths. Experimental values are from linear absorption in n-hexane [32]. Percent values are the deviations with respect to the experiment.

| Absorption Experiment [32] | | RPA INDO/S (full space) | |
|-------------------------------|-----------|-------------------------------|------|
| $\hbar\omega$, eV | f_{osc} | $\hbar\omega$, eV | |
| 3.04 | 0.015 | 2.874 | (5%) |
| 3.30 | | 3.505 | (6%) |
| 3.78 | 0.37 | 3.782 | (0%) |
| 4.06 | 0.10 | 3.924 | (3%) |
| 4.35 | | 4.287 | (1%) |
| 4.84 | | 5.031 | (4%) |
| 5.46 | 2.27 | 5.150 | (6%) |
| 5.88 | | 5.816 | (1%) |
| | | 6.008 | |
| | | 6.078 | |
| 6.36 | | 6.202 | (2%) |

High symmetry of the molecule causes the majority of states to be optically dark. Only the states of T_{1u} symmetry may have nonzero oscillator strengths and show up in linear absorption [26]. It seems that the abundance of the singlet optically dark states below the first optically allowed transitions is not fully realized. The present result may, therefore, shed some light onto a controversial issue of an apparent anomalously fast singlet-to-triplet

relaxation [26].

The problem could have been simplified by taking symmetry considerations into account *before* the RPA equations are solved. It would be, however, opposite to the purpose of this letter, which is to demonstrate in the first place the performance of the method for a complex problem. In particular, specific difficulties could have been expected from the high level of degeneracies in the spectrum. No problems of that kind have been noticed.

In conclusion, a new method is proposed for solving RPA-type equations with the computational effort comparable to that required to solve static self-consistent field equations for the ground state. The method allows to compute low-energy excitonic states at the level of theory which may be hard or impossible to achieve using conventional techniques.

As suggested in Ref. [10], calculation of the electronic excitation energy at various nuclear configurations yields effectively the excited-state adiabatic surface of the molecule, provided that the ground-state adiabatic surface is known. Thus, an ability to compute the excitation energy at computational expense comparable to the ground-state calculation can provide a long-sought opportunity to perform realistic molecular-dynamics simulations of photochemical reactions of large biological molecules.

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